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In situ nuclear-magnetic-resonance study of deformation-induced atomic diffusion in NaCl

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We show that an enhancement of diffusive atomic motion during plastic deformation can be observed by rotating-frame nuclear-spin-relaxation measurements. ^{23}Na NMR experiments were carried out as a function of temperature on NaCl single crystals during deformation at constant strain rate. Evaluation of the data yields the strain-rate and temperature dependences of the concentration of the excess vacancies accountable for the enhanced atomic diffusion. The result is discussed in view of formation and annihilation of the excess vacancies during the deformation process.

I. INTRODUCTION

Atomic diffusion in crystalline solids occurs mainly by a vacancy mechanism, i.e., the atomic jump rate Γ is controlled by the concentration c_v of vacancies according to^{1,2}

$$\Gamma = \frac{1}{\tau} = c_v \Gamma_v. \quad (1)$$

Here Γ_v denotes the jump frequency of the vacancies, which is determined by a thermally activated process:

$$\Gamma_v = \Gamma_0 \exp(-E_m/kT), \quad (2)$$

where E_m is the migration energy and Γ_0 is an attempt frequency. The diffusion coefficient D is proportional to the jump rate Γ . For isotropic diffusion one finds

$$D = \frac{a_0^2}{6} \Gamma, \quad (3)$$

where a_0 is the length of one atom jump. The coefficient D can be measured by transport experiments (radio tracer, electrical conductivity) taking into account the correlation factor of the actual diffusion mechanism.^{1,2} In ultrapure materials the vacancies are created by thermal processes, i.e., the intrinsic vacancy concentration c_v is determined by the minimal free enthalpy according to

$$c_v = \exp(S_f/K) \exp(-E_f/kT), \quad (4)$$

where S_f and E_f denote the entropy and the energy, respectively, for single-vacancy formation. For Schottky pairs, one has to replace S_f and E_f by $S_f/2$ and $E_f/2$ in Eq. (4). An additional number of vacancies, however, can be created by various effects such as quenching the sample from high temperatures, addition of impurities such as alkaline-earth ions in alkali halides and external

processes such as irradiation³ or plastic deformation.¹⁴ These excess athermal vacancies lead to an increase of the atomic jump rate Γ according to Eq. (1). In the present paper we report an investigation of the atomic jump rate in NaCl single crystals enhanced by excess vacancies created by plastic deformation at constant strain rate $\dot{\epsilon}$. The jump rate Γ is observed by ^{23}Na rotating-frame nuclear-spin-relaxation (NSR) measurements.

II. DEFORMATION-INDUCED VACANCIES

A plastic deformation of a crystalline solid with a deformation rate $\dot{\epsilon}$ is known to create an additional number of vacancies. The concentration of these excess vacancies $c_v(\dot{\epsilon})$, is given by the rate equation⁴

$$\dot{c}_v(\dot{\epsilon}) = \dot{c}_v(\dot{\epsilon})|_f + \dot{c}_v(\dot{\epsilon})|_a, \quad (5)$$

where $\dot{c}_v|_f$ is the rate of vacancy production during straining and $\dot{c}_v|_a$ is the rate of vacancy annihilation. The formation process is governed by nonconservative motion of jogs on screw dislocations:⁵

$$\dot{c}_v(\dot{\epsilon})|_f = \alpha(T, \epsilon) \dot{\epsilon}, \quad (6)$$

where $\alpha(T, \epsilon)$ is proportional to the concentration of jogs.^{4,5} The excess vacancies disappear via diffusive motion to sinks at a rate proportional to the actual vacancy concentration.

In general dislocations are assumed to be the primary vacancy sinks:

$$\dot{c}_v(\dot{\epsilon})|_a = -\beta_0 \Gamma_v \rho(\epsilon) c_v(\dot{\epsilon}), \quad (7)$$

where ρ denotes the dislocation density depending on the total plastic deformation ϵ and β_0 is a coefficient independent of $\dot{\epsilon}$ and T .

Then the steady-state condition $\dot{c}_v(\dot{\epsilon})=0$ leads to the following expression for the strain-rate-induced concen-

tration of the excess vacancies:

$$c_v(\dot{\epsilon}) = \frac{1}{\beta_0 \Gamma_0} \frac{\alpha(T, \epsilon)}{\rho(\epsilon)} \exp \left[\frac{E_m}{kT} \right] \dot{\epsilon}. \quad (8)$$

It should be noted that with the assumption of uniformly distributed dislocations the enhanced diffusion is considered to be isotropic and that the jump frequency in Eq. (7) does not depend on the direction.

III. EXPERIMENTS AND EVALUATION

The magnitude of the atomic jump rate Γ in crystalline solids can be determined by nuclear-spin-relaxation (NSR) experiments in the rotating frame.⁶ Hence, measuring Γ by means of NSR with and without deforming the sample offers the possibility of an *in situ* determination of the concentration $c_v(\dot{\epsilon})$ of the excess vacancies. The experiments were performed on ultrapure NaCl single crystals of size $11 \times 6.5 \times 6.5 \text{ mm}^3$ supplied by Dr. Korth at Kiel, Federal Republic of Germany. Spectrochemical analysis of the samples showed a concentration of about 1.5 ppm divalent cations, mostly Ca^{2+} . Hence, the samples contained a constant amount of impurity-controlled vacancies: $c_v^I = 1.5 \text{ ppm}$.

The ^{23}Na NSR rate in the rotating frame $1/T_{1\rho}$ was measured as a function of temperature, while the crystal under investigation was deformed in the $\langle 100 \rangle$ direction at a constant strain rate $\dot{\epsilon}$. The measurements were carried out in a magnetic field of 4.2 T corresponding to a Larmor frequency of 47.6 MHz by means of a NMR tensile device described in detail elsewhere.⁷ The locking field B_1 in the rotating frame was 0.22 mT. In order to observe the excess vacancies at a constant density of dislocations [$\rho(\epsilon) = \text{const}$], the $T_{1\rho}$ -measurements were performed at a constant strain ϵ of about 15% by an appropriate triggering of the $T_{1\rho}$ -pulse sequence. The increase $\Delta\epsilon$ of strain during a pulse sequence of length $\sim 10^{-2} \text{ s}$ leads to $\Delta\epsilon \approx 1.5\%$ for the maximum strain rate of 1.5 s^{-1} . Results of the experiments with ($\dot{\epsilon} = 0.4 \text{ s}^{-1}$) and without ($\dot{\epsilon} = 0$) deformation of the samples are shown in Fig. 1.

For $\dot{\epsilon} = 0$ the NSR rate consists of two contributions, namely, a phonon-quadrupole contribution $1/T_{1\rho}|_{\text{ph}}$ (dashed line) and an atomic-motion-induced contribution $1/T_{1\rho}|_{\text{diff}}$ (solid line) which considerably exceeds the phonon contribution at elevated temperatures;

$$\frac{1}{T_{1\rho}} = \frac{1}{T_{1\rho}} \Big|_{\text{ph}} + \frac{1}{T_{1\rho}} \Big|_{\text{diff}}. \quad (9)$$

According to van Kranendonk,⁸ above about half the Debye temperature the phonon contribution follows a T^{-2} -law which is marked by the dashed line.

The diffusion-induced part $(1/T_{1\rho})|_{\text{diff}}$ is determined by the spectral density $J(\omega)$ of the pair correlation function of atoms with hopping rate $\Gamma = 1/\tau$ according to⁶

$$\frac{1}{T_{1\rho}} \Big|_{\text{diff}} = \frac{\langle \omega_\rho^2 \rangle}{2\omega_{\text{eff}}} J(\omega_{\text{eff}}\tau). \quad (10)$$

Here $\langle \omega_\rho^2 \rangle$ denotes the mean-squared interaction between

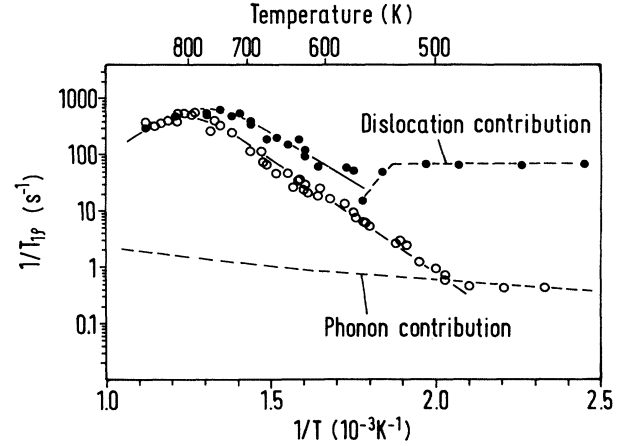


FIG. 1. ^{23}Na NSR rate $1/T_{1\rho}$ in single-crystalline NaCl vs inverse temperature without [$\dot{\epsilon}=0$ (○)] deformation and with [$\dot{\epsilon}=0.4 \text{ s}^{-1}$ (●), $\epsilon=15\%$] deformation in the $\langle 100 \rangle$ direction.

the spins in the rotating frame and $\omega_{\text{eff}} = (\gamma^2 B_1^2 + \langle \omega_\rho^2 \rangle)^{1/2}$ is the effective Larmor frequency (γ : gyromagnetic ratio of the spins). A considerable number of theoretical calculations have been performed in the past in order to determine the spectral density $J(\omega)$ of a given motional process.⁹ In the present investigation we have used the Torrey approach¹⁰ for evaluating the experimental data, i.e., $J(\omega\tau) = J_{\text{Torrey}}(\omega\tau)$. Independent of the actual approach, however a maximum in the relaxation rate $1/T_{1\rho}$ is proposed by all the theories at the temperature when $\tau(T) = (2\omega)^{-1}$.

As depicted in Fig. 1, deforming the sample with a constant strain rate $\dot{\epsilon} = 0.4 \text{ s}^{-1}$ leads to further increase of the atomic-motion-induced contribution to $1/T_{1\rho}$ between about 550 and 800, whereas at ambient temperatures an additional dislocation-induced contribution (dashed line) occurs which decreases rapidly above 525 K.¹¹ Subtracting the phonon-induced part $1/T_{1\rho}|_{\text{ph}}$ and the dislocation-induced part, respectively, from the observed $T_{1\rho}$ -data in Fig. 1, one obtains the diffusion-induced contributions to the relaxation rate $1/T_{1\rho}|_{\text{diff}}$, which are presented in Fig. 2. The solid lines in Fig. 2 are fits to the data by means of Eq. (10) using Torrey's approach for the spectral density $J(\omega)$. As expected from the Torrey theory,^{9,10} a maximum in the relaxation rate $1/T_{1\rho}$ occurs at the temperature where $2\omega_{\text{eff}}\tau = 1$. For both sets of data ($\dot{\epsilon} = 0$ and $\dot{\epsilon} = 0.4 \text{ s}^{-1}$), the strength of the coupling between the spins $\langle \omega_\rho^2 \rangle$ was found to be determined by magnetic dipole interaction between the spins and by vacancy-controlled nuclear quadrupole interaction, i.e., $\langle \omega_\rho^2 \rangle = \langle \omega_{D\rho}^2 \rangle + c_v \langle \omega_{Q\rho}^2 \rangle$. The analysis yields $\langle \omega_{D\rho}^2 \rangle = 1.35 \times 10^7 \text{ s}^{-2}$ in good agreement with the value of $1.07 \times 10^7 \text{ s}^{-2}$ valid for ^{23}Na spins in NaCl,¹² and $\langle \omega_{Q\rho}^2 \rangle = 1.13 \times 10^{13} \text{ s}^{-2}$. One should remark that the transformation $\langle \omega_\rho^2 \rangle = \frac{1}{3} \langle \omega^2 \rangle$ has to be used in order to compare the coupling strength in the rotating frame with that in the laboratory frame.⁹ Further, the effective precession frequency ω_{eff} in Eq. (10) was about 1.71×10^4

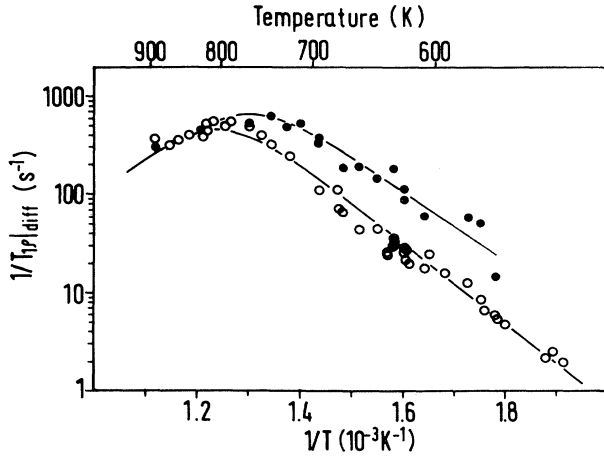


FIG. 2. Atomic-motion-induced contribution to NSR, $1/T_{1\rho}|_{diff}$ vs inverse temperature as obtained from the data of Fig. 1 by subtracting the phonon part and the dislocation-induced part. Solid lines are fits to the data by means of Torrey's approach [Eq. (10)]. [$\epsilon=0$ (\circ), $\epsilon=15\%$ (\bullet)]. As expected from the theory a maximum in the relaxation rate occurs at the temperature where $2\omega_{eff}\tau=1$.

s^{-1} , depending slightly on c_v .

For $\dot{\epsilon}=0$, in the entire temperature range the atomic jump rate Γ was found to be governed by the constant number of extrinsic cation vacancies, i.e., $c_v=c_v^I=1.5$ ppm in Eq. (1). The fit procedure yields $\Gamma_0=2.5\times 10^{15} s^{-1}$ and $E_m=0.81$ eV for the attempt frequency and migration energy, respectively. The experimental values for Γ_0 and E_m agree with that predicted using the reported diffusion data on NaCl.²

Accordingly,

$$D = \frac{a_0^2}{6} \Gamma = \frac{a_0^2}{6} \Gamma_0 c_v \exp(-E_m/kT) = D_0 c_v \exp(-E_m/kT),$$

where $D_0=3.1$ cm²/s. Thus $\Gamma_0=6D_0/a_0^2=6\times 10^{15} s^{-1}$ with $a_0=5.56\times 10^{-8}$ cm. This value for Γ_0 is three times that found experimentally.

For $\dot{\epsilon}=0.4 s^{-1}$, the total vacancy concentration is increased by the strain rate according to Eq. (8) and is given by $c_v=c_v^I+c_v(\dot{\epsilon})$. Supposing that the jump rate Γ_v of the vacancies remains unchanged by the deformation process, i.e., $\Gamma_v=2.5\times 10^{15} \exp(-0.81\text{eV}/kT) s^{-1}$ as for $\dot{\epsilon}=0$, one can perform the same fitting procedure as for the $\dot{\epsilon}=0$ data using $\Gamma=[c_v^I+c_v(\dot{\epsilon})]\Gamma_v$ instead of $\Gamma=c_v^I\Gamma_v$ in Eq. (10).

Thus, the NSR rate $1/T_{1\rho}|_{diff}$ can be written as

$$\frac{1}{T_{1\rho}} \Big|_{diff} = \frac{\langle \omega_{D\rho}^2 \rangle + [c_v^I + c_v(\dot{\epsilon})] \langle \omega_{Q\rho}^2 \rangle}{2\omega_{eff}} \times J_{\text{Torrey}} \left[\frac{\omega_{eff}}{\Gamma_v [c_v^I + c_v(\dot{\epsilon})]} \right]. \quad (10a)$$

Obviously, the only fitting parameter in Eq. (10a) is the

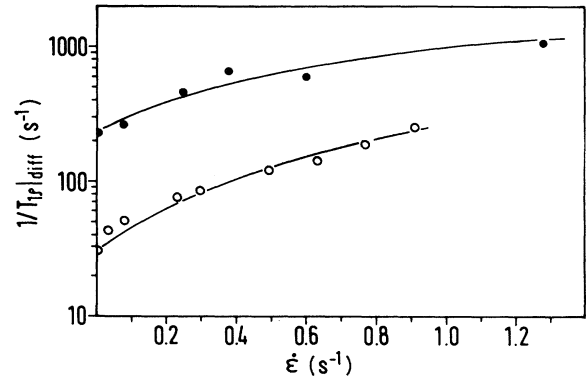


FIG. 3. Atomic-motion-induced contribution to ^{23}Na NSR, $1/T_{1\rho}|_{diff}$ vs strain rate for two different temperatures [623 K (\circ); 723 K (\bullet)]. Solid lines are fits to the data by means of the same approach used in Fig. 2.

excess vacancy concentration $c_v(\dot{\epsilon})$.

In order to obtain further information about the strain-rate dependence of $c_v(\dot{\epsilon})$ we have carried out additional $T_{1\rho}$ -measurements as a function of strain rate $\dot{\epsilon}$ at two different temperatures (623 and 723 K) as depicted in Fig. 3. The excess vacancy concentration $c_v(\dot{\epsilon})$, during deformation was extracted from all the experimental data using Eq. (10a). The solid lines in Figs. 2 and 3 are the corresponding fits to the data by means of Eq. (10a), which resulted in a linear increase of the excess vacancy concentration $c_v(\dot{\epsilon})$ with strain rate $\dot{\epsilon}$

$$c_v(\dot{\epsilon}) = (6.27 \pm 0.14) \times 10^{-7} \times \exp[(0.10 \pm 0.03 \text{ eV})/kT] \dot{\epsilon} / s^{-1}. \quad (11)$$

This experimental finding is in agreement with the model [Eq. (8)], where the excess vacancy concentration was shown to be linearly dependent on $\dot{\epsilon}$. In order to demon-

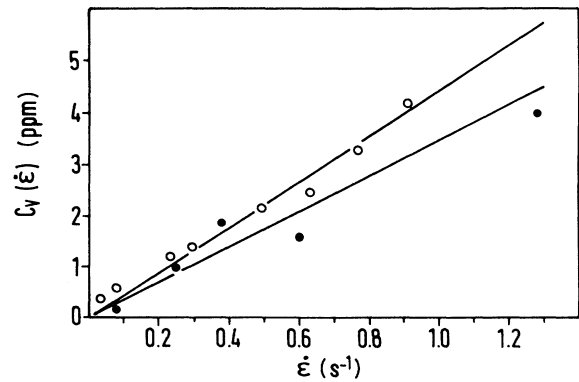


FIG. 4. Strain-rate dependence of the deformation-induced excess vacancy concentration, $c_v(\dot{\epsilon})$, for two different temperatures [623 K (\circ), 723 K (\bullet)] as obtained from the data of Fig. 3. The straight lines representing the result of the total fit procedure (solid lines in Figs. 2 and 3) are given by Eq. (11).

strate the experimental errors more clearly, the correlation between the experimental results and Eq. (11) is depicted in Fig. 4 for the two test temperatures.

IV. DISCUSSION

As expected from Eq. (8) the excess vacancy concentration $c_v(\dot{\epsilon})$ [Eq. (11)] was found to increase linearly with rising $\dot{\epsilon}$, indicating that a first-order mechanism occurs for annihilation of vacancies as proposed by Eq. (7). Further, $c_v(\dot{\epsilon})$ was found to depend Arrhenius-like on temperature in accord with Eq. (8). However, the experimentally observed energy of 0.10 eV in Eq. (11) differs strongly from the migration energy $E_m = 0.81$ eV of cation vacancies in Eq. (8). One should note here that, because of charge compensation in alkali halides, principally pairs of cation and anion vacancies are created by the deformation process. It is well known, however, that in the temperature range of interest the atomic diffusion is primarily governed by the cation vacancies.² Comparing the experimental finding with the value for the migration energy of cation vacancies, one has to conclude that the process of vacancy formation [$\alpha(T, \epsilon)$ in Eq. (6)] also varies exponentially with temperature, i.e., $\alpha(T, \epsilon) = \alpha_0(\epsilon) \exp(-E^*/kT)$ with $E^* = 0.71$ eV. As discussed in Sec. II, the nonconservative motion of jogs on screw dislocations is assumed to be responsible for the vacancy-formation process. If the jogs are thermally created, the energy E^* should be equal to that for formation of jogs E_j , which can be estimated according to Seeger¹³ by $E_j \approx \mu b^3/10$ (μ is the shear modulus, and b is the magnitude of the Burgers vector). Using the values for the shear modulus given by Raj, Phar, and Whitten-

berger¹⁵ one obtains for the jog-formation energy

$$E_j(T) = (0.70 - 3.965 \times 10^{-4} T/K) \text{ eV} . \quad (12)$$

With the assumptions made above, together with Eqs. (8) and (12), one finds for the deformation-induced vacancy concentration

$$c_v(\dot{\epsilon}) = \frac{\alpha_0(\epsilon)}{\beta_0 \rho(\epsilon) \Gamma_0} \exp \left[\frac{3.965 \times 10^{-4} \text{ eV/K}}{k} \right] \times \exp \left[\frac{0.11 \text{ eV}}{kT} \right] \dot{\epsilon} . \quad (13)$$

The observed agreement of this result with the experimental findings in Eq. (11) supports the assumption that excess vacancies are formed by thermally created dislocation jogs.

Estimations based on this novel approach show that an *in situ* observation of excess vacancies under deformation should also be possible in metals where the vacancies are intrinsic in nature for $\dot{\epsilon} = 0$. We are currently performing initial experiments on aluminum foils using ²⁷Al as the nuclear probe. Finally, it should be remarked that the $T_{1\rho}$ experiments described here should also allow *in situ* observation of details of the enhanced atomic diffusion by excess vacancies created by irradiation (for instance, neutron irradiation) of the sample under investigation.

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